ing to a mercury bubbler, are placed powdered pyridinium chlorochromate (26 g, 120 mmol) and methylene chloride (200 mL). To the well-stirred suspension, a solution of trioctylaluminum in THF thus prepared was added with the aid of a double-ended needle. The mixture was stirred at room temperature for 1 h. Then, ethyl ether (200 mL) was added and the mixture was filtered through a column containing Florisil®. The solid residue in the flask was triturated with ethyl ether (3×50 mL) and filtered through the same Florisil column. The combined filtrate was concentrated and distilled to afford 6.04 g of pure octanal (78%); bp 170-172 °C/761 mmHg. The purity was further confirmed by GC analysis.

A small scale of same reaction (trioctylaluminum, 1 mmol) was also performed and tridecane was added as an internal standard. The product aldehyde was analyzed by GC with use of a Carbowax TAP capillary column (25 m) to show 97% octanal formation.

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The Synthesis of a New Pyrazolylimidazolinone *via* 1,3-Dipolar Cycloaddition Reaction of *N*-Methyl Sydnone with Methyl Propiolate

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Herbicides having imidazolinone moiety, such as *imazapyr* and *imazethapyr*, have attracted much attention as a potent herbicidal activity, inhibiting branched chain amino acid biosynthesis.[1] In search for new structures with good biological activities, we have extensively studied on the modification of *imazapyr* and designed the pyrazolylimidazolinone (**1**) as a target molecule (Scheme 1).

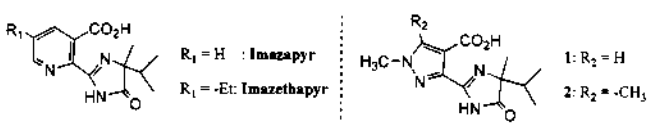
Although the compound **2** (R_2=CH_3) had already been reported,[2] we expected that the compound **1** (R_2=H) would show better herbicidal effect than **2** due to the structure-activity correlation calculations.[3]

As we realized that it was difficult for the synthesis of **1** by the route employed in the synthesis of **2**, we explored a new procedure using 1,3-dipolar cycloaddition reaction of *N*-methylsydnone (**3**) with methyl propiolate.

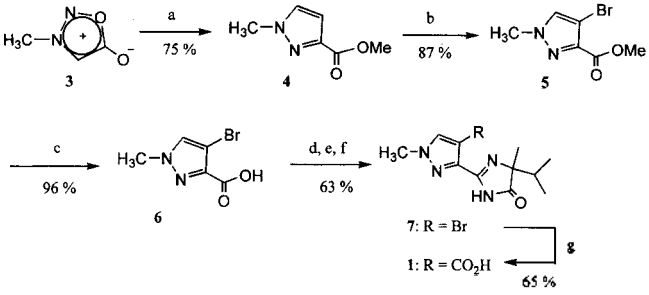
It have been known that sydnones, known as meso-ionic heterocycles,[4] undergo well 1,3-dipolar cycloaddition reaction with alkyl propiolates to give pyrazoles of two possible regioisomers and 3-pyrazolecarboxylate is predominantly formed over 4-pyrazolate.[5]

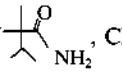
When a mixture of *N*-methylsydnone (**3**) and methyl propiolate were refluxed in toluene for 12h,[6] only methyl 1-methyl-3-pyrazolecarboxylate was obtained with good regioselectivity in 75% yield. We conceived the product of dipolar cycloaddition reaction is methyl 1-methyl-3-pyrazolecarboxylate of possible two regioisomers, methyl 1-methyl-3-pyrazolecarboxylate and methyl 1-methyl-4-pyrazolecarboxylate, by its appropriate coupling of two protons (J=2.5 Hz) at the pyrazole ring in ^{1}H NMR spectrum.

Compound **4** could be converted to 4-bromopyrazole **5** with good regioselectivity. This conversion which was confirmed by the disapperence of the peak at 6.82 ppm in ^{1}H NMR of **4** was carried out by treatment with NBS in chloro-



Scheme 1



Scheme 2. *Reagents and conditions*: [a] methyl propiolate, toluene, reflux, 12h. [b] NBS/$CHCl_3$, reflux, 5h. [c] LiOH/MeOH/H_2O, rt, overnight. [d] $SOCl_2$, reflux, 3h. [e]  , CH_3CN. [f] NaOH/EtOH/H_2O, reflux, 2h. [g] 2.2 eq. n-BuLi/THF, −78 °C, 20 min, then, CO_2, −78 °C, rt.

form under reflux in 87% yield. Ester group of **5** was easily hydrolyzed by lithium hydroxide in a mixed solvent of methanol and water at room temperature in 96% yield. Carboxylic acid **6** was converted to acyl chloride by refluxing in thionyl chloride for 3 h, and then, reacted with 2-amino-2, 3-dimethyl butyramide in acetonitrile to give the amide product. The cyclization of the amide was achieved by sodium hydroxide treatment in a mixed solvent of ethanol and water with heating for 2 h to afford the imidazolinone **7** in 63% overall yield. Lithium-bromine exchange of **7** with *n*-butyllithium and the subsequent carboxylation by treatment with carbon dioxide afforded the target molecule **1**.[7]

In summary, thermally induced 1,3-dipolar cycloaddition reaction of *N*-methylsydnone (**3**) with methyl propiolate gave methyl 1-methyl-3-pyrazolecarboxylate with good regioselectivity and a new pyrazolylimidazolinone **1** has been synthsized using the cycloaddut **4** as a key intermediate. Further studies on the synthesis of other pyrazolylimidazolinone derivatives and their herbicidal activity evaluation are in progress.

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7. The ^{1}H NMR data of the key intermediary products are as follows; **1** (200 MHz, MeOH-d_4): δ 8.41 (1H, s, Ar), 4.13 (3H, s, N-CH_3), 2.17 (1H, quintet, *J*=7 Hz), 1.53 (3H, s, -CH_3), 1.17 (3H, d, *J*=7 Hz, -CH_3), 0.94 (3H, d, *J*=7 Hz, -CH_3). **4** (200 MHz, $CDCl_3$): δ 7.39 (1H, d, *J*= 2.4 Hz), 6.82 (1H, d, *J*=2.4 Hz), 3.98 (3H, s, O-CH_3), 3.92 (3H, s, N-CH_3). **5** (200 MHz, $CDCl_3$): δ 7.49 (1H, s, Ar), 3.98 (3H, s, O-CH_3), 3.95 (3H, s, N-CH_3). **7** (200 MHz, $CDCl_3$): δ 8.31 (1H, brs, NH), 7.49 (1H, s, Ar), 3.93 (3H, s, N-CH_3), 2.08 (1H, quintet, *J*=7 Hz), 1.40 (3H, s, -CH_3), 1.04 (3H, d, *J*=7 Hz, -CH_3), 0.89 (3H, d, *J*=7 Hz, -CH_3).

(Salen)Mn(III) Catalyzed Oxidation of Alcohols Using Sodium Hypochlorite as an Oxidant

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Recently, (salen)Mn(III) complexes have attracted attention as efficient catalysts for the epoxidation of olefins.[1] Most of the studies in this area has been devoted to utilize chiral (salen)Mn complexes to effect enantioselective olefin epoxidation with different types of oxidants. Even though (salen)Mn complexes have a high potential in organic synthesis primarily due to their easy preparation and handling, relatively few results have been reported on the subjects other than epoxidation chemistry.[2] Recently, we have reported that benzylic hydrocarbons can be oxidized to the corresponding carbonyl compounds using (salen)Mn catalysts.[3] In this procedure, we assumed that the carbonyl compounds were formed through the alcohols as the intermediates. Therefore, we were forced to examine alcohols as the substrates in (salen)Mn-mediated oxidation process.

The alcohol oxidation was conducted using sodium hypochlorite[4] which is regarded as the most pratical oxidant in (salen)Mn mediated oxidation procedure. In Table 1, the results of the different reaction conditions for the conversion of 1-phenylethanol to acetophenone are summarized. Control experiment showed that the (salen)Mn catalysts were essential for the oxidation of 1-phenylethanol under the reaction conditions (entry 1). Among the racemic (salen) Mn complexes[5] examined, the complex **1** was found to be the most efficient catalyst for the oxidation of the alcohol (entries 2-5). Although the higher reactivity of (salen)Mn **1** compared to other complexes is not clear, but the combination of electronic and steric environments around the salen ligand would account for the reactivity difference.[6] This reaction was also found to be dependent on the amount of catalysts and oxidant employed. With the catalytic amount (8 mol %) of the complex **1**, it was observed that four equivalent of the oxidant was necessary to achieve the complete conversion of the starting material. This could be explained by assuming that, because this reaction proceeds under biphasic conditions, the mass transport of the aqueous HOCl into the organic layer becomes the rate-determining step, as already shown in the analogous epoxidation procedure.[7] Thus, excess amount of the aqueous oxidant facilitates the catalytic cycle, which makes the reac-